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FACILE CLEAVAGE OF THE MO=MO BOND IN REACTIONS BETWEEN (MO2(OBU--ETC(U)
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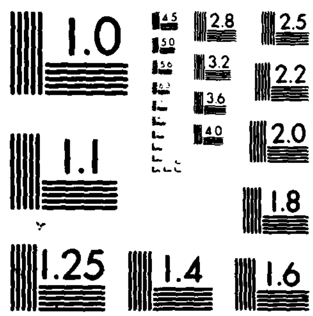

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FACILE CLEAVAGE OF THE Mo≡Mo BOND IN REACTIONS BETWEEN $Mo_2(OBu^t)_6$ AND ARYL AZIDES AND MOLECULAR OXYGEN

by

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Hydrocarbon solutions of $Mo_2(OBu^t)_6$ react with arylazides and molecular oxygen at room temperatures according to equations ~~1 and 2, shown below~~. I is structurally related to $[MoMe_2(NBu^t)_2]_2$ recently characterized by Nujent and Harlow (~~J. Am. Chem. Soc. 1980, 102, 1759~~); II, the tert-butyl ester of molybdic acid, is the first molecule of its kind to be prepared for the group

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6 transition elements.

1 $$Mo_2(OBu^t)_6 + 4ArN_3 = [Mo(OBu^t)_2(NAr)_2]_2 + 4N_2 + 2Bu^tOH$$

I

where Ar = phenyl and p-tolyl

2 $$Mo_2(OBu^t)_6 + 2O_2 = 2Mo(O)_2(OBu^t)_2 + 2Bu^tOH$$

II

FACILE CLEAVAGE OF THE Mo≡Mo BOND IN REACTIONS

BETWEEN $Mo_2(OBu^t)_6$ AND ARYL AZIDES AND MOLECULAR OXYGEN

Sir:

Recently, it has been shown that Mo-Mo multiple bonds can be cleaved under mild conditions by the addition of strong π-acceptor ligands. Specifically, Walton and coworkers[1-3] have shown that isocyanide ligands destroy the M≣M bond in a number of Mo_2^{4+} containing compounds yielding mononuclear $Mo(CNR)_7^{2+}$ compounds and we have found related reactions involving the Mo≡Mo bond in Mo_2^{6+} containing compounds with carbon monoxide[4] and nitric oxide.[5] We wish here to report two reactions of a different nature which proceed, under very mild conditions, to disrupt the Mo≡Mo bond in $Mo_2(OBu^t)_6$.[6] This work provides further evidence of the high susceptibility of the M≡M bond to attack by a wide variety of substrates[7] and, in one of the present instances, leads to the formation of a mononuclear compound, $Mo(O)_2(OBu^t)_2$, which may be viewed as the tert-butyl ester of molybdic acid, the first molecule of its kind to be prepared for the group 6 transition elements.

Hydrocarbon solutions of $Mo_2(OBu^t)_6$ react[8] with arylazides and molecular oxygen at room temperatures according to equations 1 and 2, shown below.

1 $$Mo_2(OBu^t)_6 + 4ArN_3 = \underset{\text{I}}{[Mo(OBu^t)_2(NAr)_2]_2} + 4N_2 + 2Bu^tO\underline{H}$$

where Ar = phenyl and p-tolyl

2 $$Mo_2(OBu^t)_6 + 2O_2 = \underset{\text{II}}{2Mo(O)_2(OBu^t)_2} + 2Bu^tO\underline{H}$$

The tert-butanol is evidently formed from a hydrogen atom abstraction reaction involving Bu^tO and solvent molecules: reaction 2, when carried out in 1,3-cyclohexadiene, yielded benzene and tert-butanol. The reaction between $Mo_2(OBu^t)_6$ and aryl azides has a parallel in the formation of the imido ligand with known reactions involving mononuclear transition metal complexes and aryl azides.[9] A single crystal structural determination[10] showed that I adopts a structure akin to that recently found[11] for $[Mo(CH_3)_2(NBu^t)_2]_2$ which provided the first structurally characterized example of a compound having unsymmetrical bridging imido ligands. A further comparison with the structures found for $Mo_2(OPr^i)_8$[12] and $Mo_2(OPr^i)_6(NO)_2$[5] is interesting. See Figure 1. In all three compounds, the molybdenum atoms are in distorted trigonal bipyramidal environments and the bridging ligands form alternately long (axial) and short (equatorial) bonds.

$Mo(O)_2(OBu^t)_2$ is a yellow liquid at room temperature, which distills in vacuo at 55°C, 10^{-4} torr and is monomeric in benzene as determined by a cryoscopic molecular weight determination. The monomeric nature of this compound in benzene is further supported by the natural abundance ^{17}O nmr spectrum which shows a single sharp signal (width at half height ~90 Hz) at 862 ppm relative to $H_2{}^{17}O$.[13] This value is well within the range observed for terminal oxo-molybdenum(VI) groups. Indeed, according to the Miller and Wentworth[14] correlation of ^{17}O chemical shifts with Mo-O bond distances, we calculate Mo-O = 1.71 Å for the oxo ligands in $Mo(O)_2(OBu^t)_2$.[15]

Malcolm H. Chisholm, Kirsten Folting
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and Molecular Structure Center
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Bloomington, Indiana 47405

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1. Brant, P.; Cotton, F.A.; Sekutowski, J.C.; Wood, T.E.; Walton, R.A. J. Am. Chem. Soc. 1979, 101, 6588.

2. Wood, T.E.; Deaton, J.C.; Corning, J.; Wild, R.E.; Walton, R.A. Inorg. Chem. 1980, 19, 2614.

3. The addition of NO to dichloromethane solutions of $Mo_2X_4L_4$ compounds, where X = Cl or Br and L = $PEtPh_2$, PEt_3 or $PBu^n{}_3$ and $Mo_2X_4(L\text{-}L)_2$ where X = Cl or NCS and LL = $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2) gives the 18 electron mononuclear compounds $Mo(NO)_2X_2L_2$ and $Mo(NO)_2X_2(L\text{-}L)$: Nimry, T.; Urbancic, M.A.; Walton, R.A. Inorg. Chem. 1979, 18, 691.

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7. For recent reviews of the chemistry surrounding the Mo_2^{6+} unit, see Chisholm, M.H.; Cotton, F.A. Acc. Chem. Res. 1978, 11, 356; Chisholm, M.H. Transition Metal Chemistry 1978, 3, 351.

8. Anhydrous solvents and dry and oxygen-free atmospheres were maintained for 1; dry solvents and dried molecular oxygen were used in 2. The compounds I and II are highly moisture sensitive and must be handled under rigorously anhydrous conditions. Satisfactory elemental analyses were obtained. Evolution and uptake of gases were followed by gas-burette.

9. Nujent, W.A.; Haymore, B.L. Coord. Chem. Rev. 1980, 31, 123 and references therein.

10. Crystal data collected at -170°C using MoKα radiation gave the following: a = 10.789(2), b = 25.904(6), c = 13.007(3) Å, α = 73.11(1), β = 81.34(1), γ = 91.25(1)°, Z = 3; d_{calcd} = 1.314 g cm^{-3}. In the space group $P\bar{1}$, there are 1½ unique molecules. Of 9734 reflections measured in the range $6^{\circ} \leq 2\theta \leq 45^{\circ}$, 8946 were unique. The structure was solved by Patterson and Fourier techniques. Full matrix refinement, in which the metal atoms were assigned anisotropic thermal parameters and all other non-hydrogen atoms isotropic parameters, converged to R(F) = 0.076 and Rw(F) = 0.086. The molecule shown in Figure 1 is the one possessing no crystallographic symmetry. Molecule 2, which possesses a center of symmetry, is virtually identical.

11. Nujent, W.A.; Harlow, R.L. J. Am. Chem. Soc. 1980, 102, 1759.

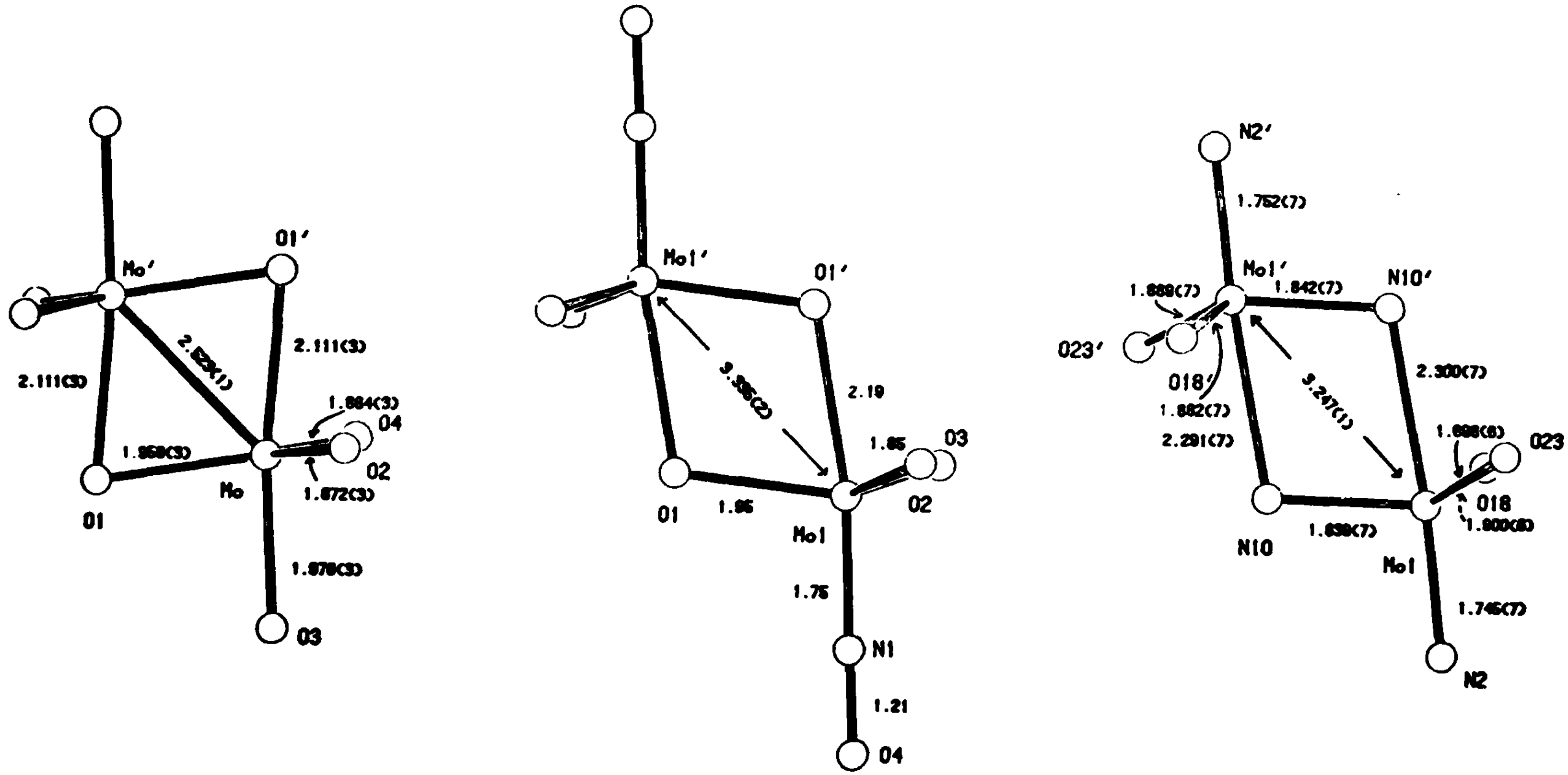
12. Chisholm, M.H.; Cotton, F.A.; Extine, M.W.; Reichert, W.W. Inorg. Chem. 1978, 17, 2944.

13. Klemperer, W.G. Angew. Chem. Int. Ed. Engl. 1978, 17, 246.

14. Miller, K.F.; Wentworth, R.A.D. Inorg. Chem. 1979, 18, 984.

15. For the absence of analogous compounds of the group 6 transition elements, see Cotton, F.A.; Wilkinson, G. "Advanced Inorganic Chemistry" 4th Ed., 1980, John Wiley Interscience Publishers. We thank the Office of Naval Research, the National Science Foundation and the Wrubel Computing Center, Indiana University for financial support. MHC is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant, 1979-84.

Caption to Figure 1: Comparison of the central skeletons of the $Mo_2(OPr^i)_8$ (left), $[Mo(NO)(OPr^i)_3]_2$ (center) and $[Mo(NC_7H_8)_2(OBu^t)_2]_2$ (right) molecules. The terminal imido ligands in $[Mo(NC_7H_8)_2(OBu^t)_2]_2$ have Mo-N-C angles = 175° (average); the Mo-N-O angle in $[Mo(NO)(OPr^i)_3]_2$ is 178°.



Mo'
O1'
2.111(3)
2.111(3)
2.528(1)
1.884(3)
O4
O2
1.958(3)
1.872(3)
O1
Mo
1.878(3)
O3
Mo1'
O1'
3.335(2)
2.19
1.85
O3
O2
O1
1.95
Mo1
1.75
N1
1.21
O4
N2'
1.752(7)
Mo1'
1.889(7)
1.842(7)
N10'
O23'
3.247(1)
2.300(7)
O18'
1.882(7)
2.291(7)
1.898(8)
O23
O18
1.900(8)
N10
1.839(7)
Mo1
1.745(7)
N2

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BETWEEN $Mo_2(OBu^t)_6$ AND ARYL AZIDES AND MOLECULAR OXYGEN

Abstract

Hydrocarbon solutions of $Mo_2(OBu^t)_6$ react with arylazides and molecular oxygen at room temperatures according to equations **1** and **2**, shown below.

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